

Urea Derivatives Enhance the Photocatalytic Activity of Dye-modified Titaniumdioxide

Stefan Földner,^a Tatiana Mitkina,^a Tobias Trottmann,^a Alexandra Frimberger,^a Michael Gruber^b and Burkhard König^{a}*

^a*Institute of Organic Chemistry, University of Regensburg, Universitätsstr. 31, 93040 Regensburg, Germany*

^b*Department of Anaesthesia, University Hospital Regensburg, Regensburg, 93051, Germany*

Supporting Information

	Page
1 Synthesis of the sensitizing dye complex N3	S-2
2 Photocatalytic reductions	S-2
3 Exemplary gas-chromatographic analyses of photo-reductions	S-4
4 Exemplary GC/MS analyses of photoreductions	S-5_Toc271568008
5 Photon-Conversion-Efficiency	S-7

1. Synthesis of the sensitizing dye complex N3

Dye complex N3 has been synthesized as described in literature.¹

2. Photocatalytic reductions

Common

TEOA (300 mg, $2 \cdot 10^{-3}$ mol), urea derivative (stock solution), starting material ($2 \cdot 10^{-4}$ mol), immobil. TiO₂ (50 mg) and 2.5 ml acetonitrile were placed in the reaction vial, sealed with a septum and cooled by liquid nitrogen. The mixture was allowed to warm up to room temperature under 50 mbar and flushed with nitrogen. This procedure was repeated one time, then the cell was irradiated under stirring for 24 h with the high power LED (530 nm, 3 Watts electrical power, 80 lumen).

For analyzing, 500 μ l of the reaction mixture were taken out directly by Eppendorf pipette and mixed with 500 μ l of a standard (toluene). 1 μ l of this solution was injected in the GC or GC/MS. The signals were integrated from the chromatogram.

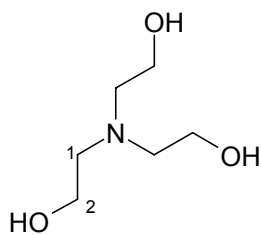
Kinetic measurements

TEOA (300 mg, $2 \cdot 10^{-3}$ mol), urea derivative (stock solution), starting material ($2 \cdot 10^{-4}$ mol), immobil. TiO₂ (50 mg) and 2.5 ml acetonitrile were placed in the reaction vial, sealed with a septum and cooled by liquid nitrogen. The mixture was allowed to warm up to room temperature under 50 mbar and flushed with nitrogen. This procedure was repeated one time, then the cell was irradiated under stirring for 24 h with the high power LED (530 nm, 3 Watts electrical power, 80 lumen).

For analyzing, 20 μ l of the reaction mixture were taken out directly by a Hamilton syringe and mixed with 20 μ l of a standard (toluene). 1 μ l of this solution was injected in the GC. The signals were integrated from the chromatogram.

Deuteration experiments

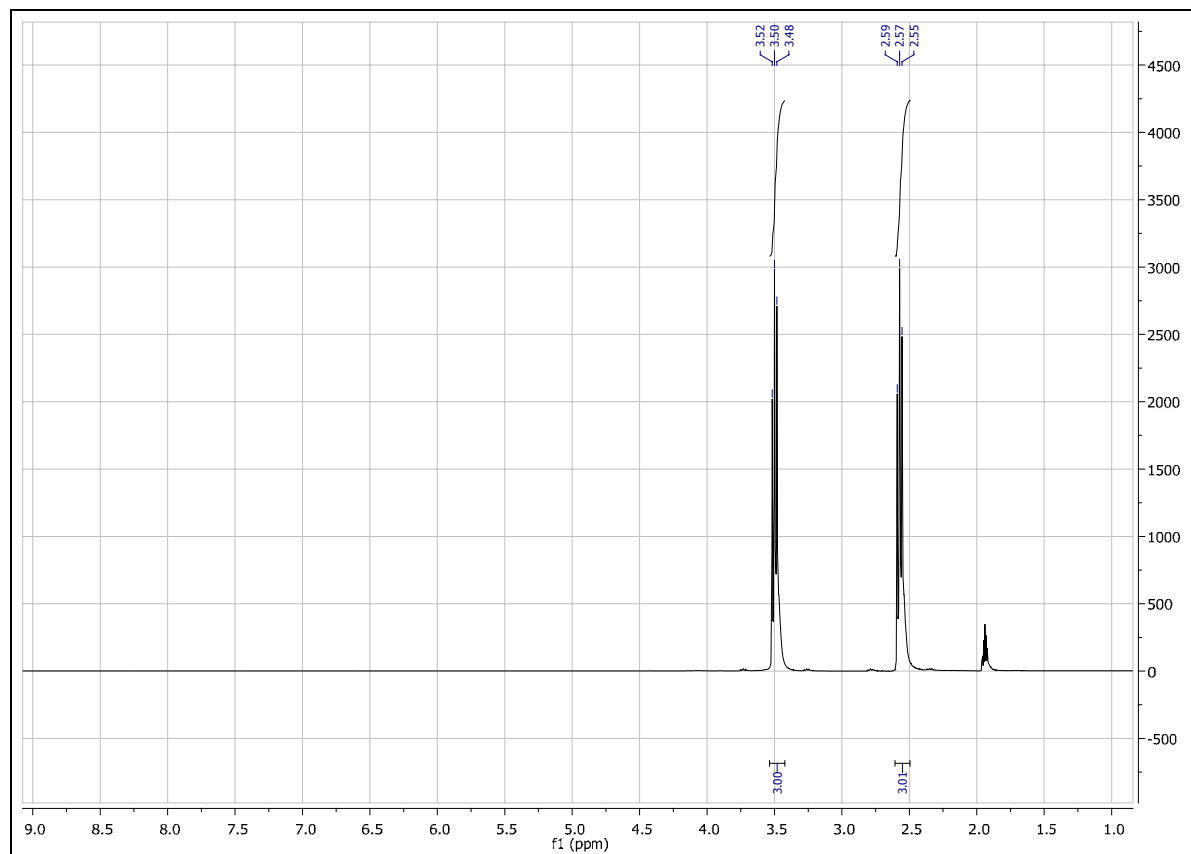
¹ (a) S. Chen, K. Kimura, *J. Phys. Chem. B* **2001**, *105*, 5397-5403. (b) E. Kolwaska, H. Remita, C. Colbeau-Justin, J. Hupka, J. Belloni, *J. Phys. Chem. C* **2008**, *112*, 1124-1131. (c) J. I. L. Chen, E. Loso, N. Ebrahim, G. A. Ozin, *J. Am. Chem. Soc.* **2008**, *130*, 5420-5421.



3

TEOA (2 g, $13 \cdot 10^{-3}$ mol) was dissolved in 2.5 ml D_2O , frozen by liquid nitrogen and lyophilized. The procedure was repeated three times and the remaining colourless oil was checked by 1H -NMR-spectroscopy.

1H NMR (300 MHz, CD_3CN , 25 °C, TMS): δ = 2.57 (t, J = 7.1 Hz, 6 H, 2-H), 3.50 (t, J = 7.1 Hz, 6 H, 1-H).



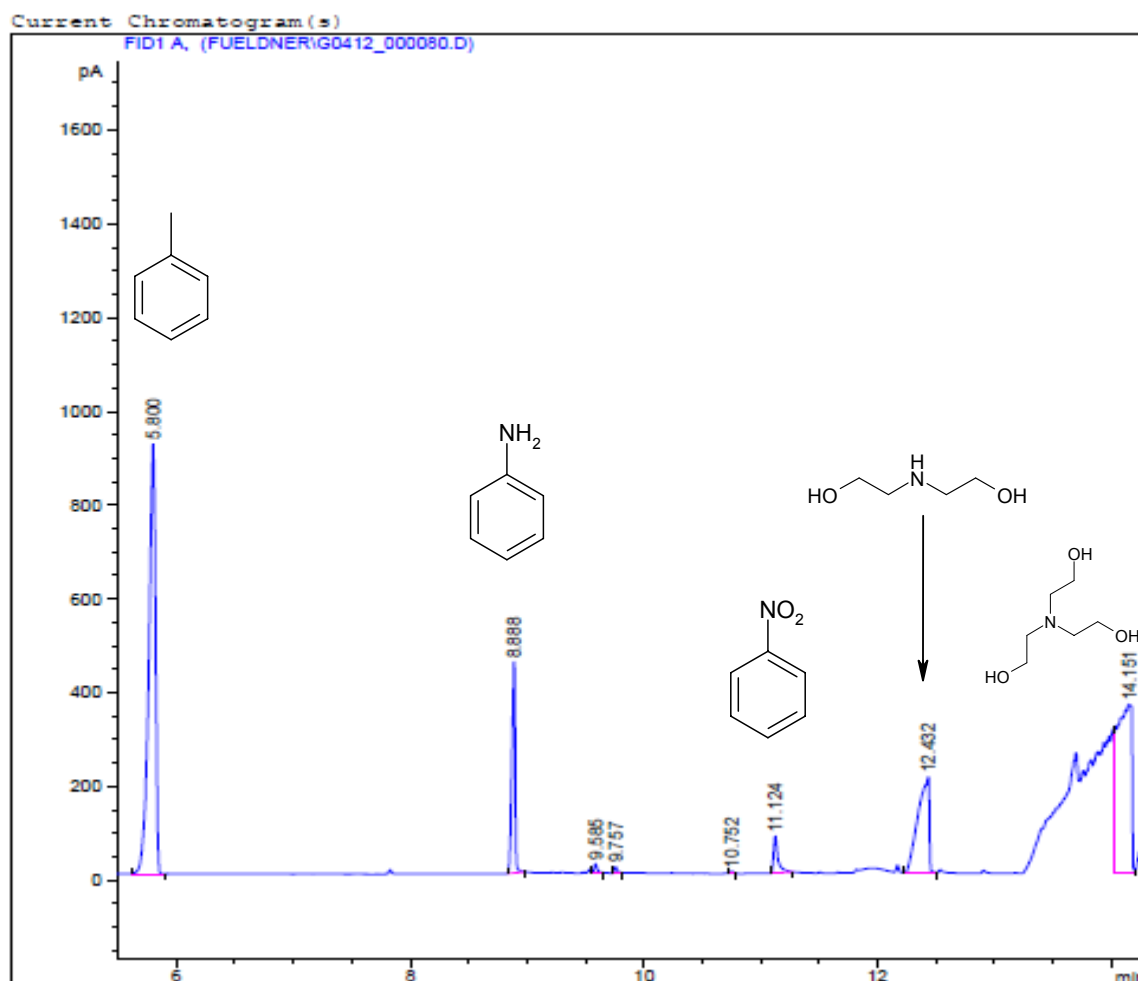
TEOA-D3 (305 mg, $2 \cdot 10^{-3}$ mol), urea derivative (stock solution), starting material ($2 \cdot 10^{-4}$ mol), immobil. TiO_2 (50 mg) and 2.5 ml acetonitrile were placed in the reaction vial, sealed with a septum and cooled by liquid nitrogen. The mixture was allowed to warm up to room temperature under 50 mbar and flushed with nitrogen. This procedure was repeated one time,

then the cell was irradiated under stirring for 24 h with the high power LED (530 nm, 3 Watts electrical power, 80 lumen).

For analyzing, 500 μl of the reaction mixture were taken out directly by Eppendorf pipette and mixed with 500 μl of a standard (toluene). 1 μl of this solution was injected in the GC/MS. The signals were integrated from the chromatogram.

3. Exemplary gas-chromatographic analyses of photo-reductions

Toluene was used as internal standard in all cases.

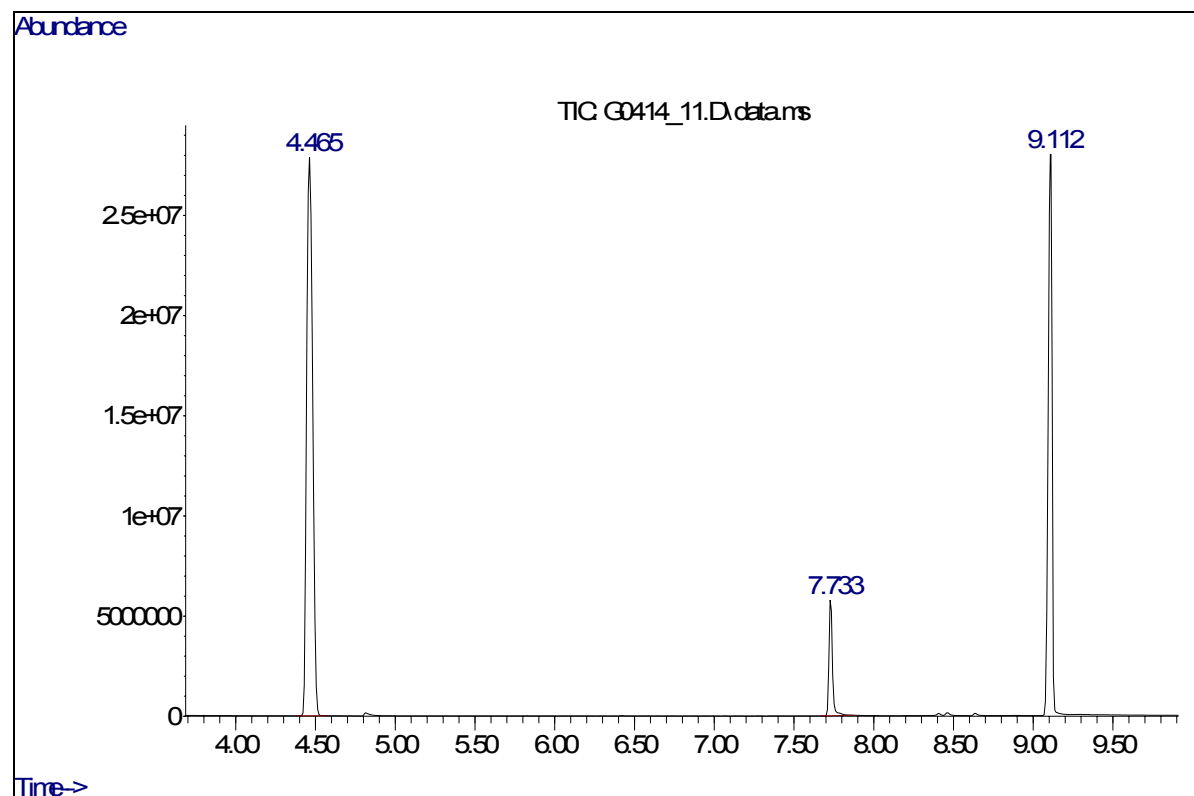


A GC 6890 Series from Agilent was used. Injection-temperature (splitinjection: 40:1 split) was at 250 °C, detection temperature was at 300 °C (FID). The column was a capillary column from J+W Scientific - DB-5MS / 30 m X 0.25m / 0.25 μm film. Helium was used as carrier gas with a flow of 1 mL/ min. Data acquisition and evaluation was done by using the software Agilent ChemStation Rev.A.06.03. (509).

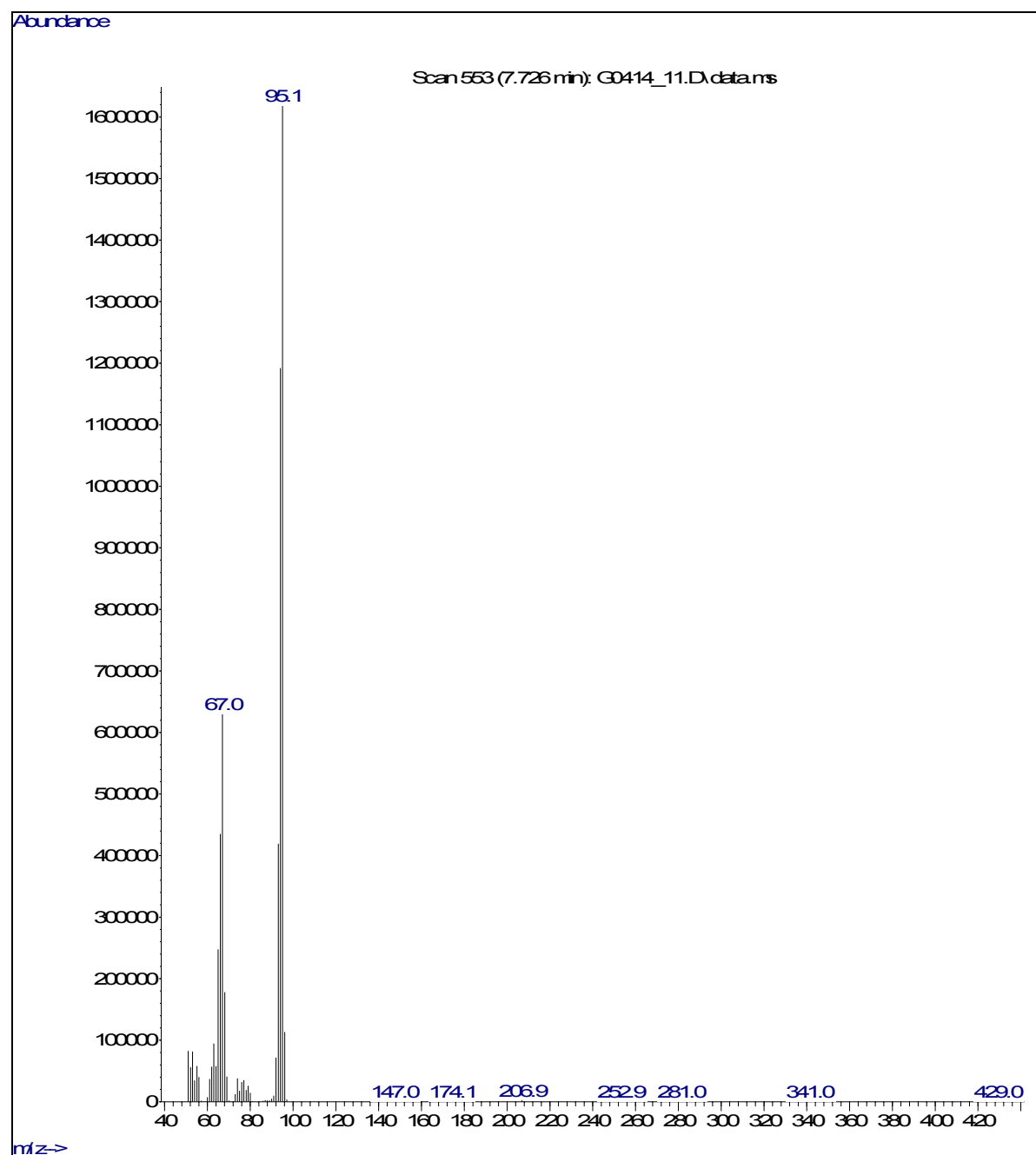
GC- and GC-MS-measurements were made and investigated while integrating the signals obtained. The GC oven temperature program adjustment was as follows:

The initial temperature was 40 °C. This was kept for 3 minute and then increased constantly at a rate of 15 °C/min for 16 minutes. The final temperature of 280 °C was kept for 5 minutes.

4. Exemplary GC/MS analyses of photoreductions



GC-Chromatogram of the conversion of nitrobenzene to deuterated aniline via TEOA-D3, dye-sensitized TiO₂ and without any catalyst after 14 h of irradiation: toluene t = 4.465 min, deuterated aniline t = 7.733 min and nitrobenzene t = 9.112 min.



Mass spectrum of peak $t = 7.733$ min of the GC-chromatogram above.

A 5973 MSD from Agilent Technologies was used. Injection-temperatures (split injection: 40:1 split) was at 300 °C, detection temperature was at 350 °C (FID). The column was a capillary column from Agilent 199091S-433 HP-5MS / 30 m X 0.25m / 0.25 μm film. Helium was used as carrier gas with a flow of 44.1 mL/ min. Data acquisition and evaluation was done by using the software MSD ChemStation D.01.02.16.

6. Photon-Conversion-Efficiency

The optimum amount for a maximum photon-conversion-efficiency was investigated as followed: N3-sensitized TiO₂ (10 mg) were placed in a UV-Vis cuvette and suspended in 2 mL MeCN. The cuvette was placed in the described apparatus,²⁷ irradiated with a high-power LED (530 nm, 1 Watts, 80 lumen) and the light intensity of the out coming light behind the sample was checked by solar cell. The procedure was repeated for different amounts of N3-sensitized TiO₂: 20, 30, 40, 50, 60, 45 and 55 mg.

Table 3: Dependencies of amount of N3-TiO₂ and light-absorption in reaction solution.

Amount N3-TiO ₂ [mg]	P _{el.} [mW] ^a
0	20.5
10	15.4
20	12.8
30	8.5
40	2.1
45	0.9
50	0.1
55	0
60	0

^a Determined according to literature.²⁷

The photon-conversion-efficiency was determined as described.² A cuvette was sealed with a septum and evacuated with vacuum of 50 mbar, flushed with nitrogen and again evacuated. This procedure was repeated 10 times. N3-sensitized TiO₂ (50 mg) was placed in the cuvette under a nitrogen stream and a solution (dried by freeze-pump-thaw procedure in a extra Schlenk-flask) of TEOA (300 mg, 2·10⁻³ mol), nitrobenzene (400 μL 0.5 M stock solution, 2·10⁻⁴ mol), catalyst stock solution and 2 mL dried MeCN was transferred into the cuvette under a nitrogen stream. The solution was irradiated with a high power LED (530 nm, 1 Watts, 80 lumen) in the described apparatus, after 36 h 100 μL were diluted with 100 μL standard solution (toluene in MeCN, 6.7·10⁻² M) and 800 μL MeCN and 1 μL was injected into the GC. The signals from the resulting chromatogram were integrated, the amount of aniline was calculated and the photon-conversion-efficiency was calculated as described.

² R. Lechner, B. König, *Synthesis* **2010**, *10*, 1712-1718.